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# Reaction of Bis(2-chloroethyl)-2-nitroethynylphosphonate with Diazoacetic Ester

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**Abstract**—Reactions of 1,3-dipolar cycloaddition of bis(2-chloroethyl)-2-nitroethenylphosphonate to methyl and ethyl diazoacetates proceed with the formation of a mixture of regioisomers of phosphorylated nitropyrazoline carboxylates that under the reaction conditions undergo isomeric transformations and denitration and afford a mixture of $\Delta^1$- and $\Delta^2$-pyrazoline- and pyrazolecarboxylates. Structures of the synthesized substances are studied by the methods of IR and $^1$H, $^{31}$P NMR spectroscopy and partially by X-ray structural analysis.
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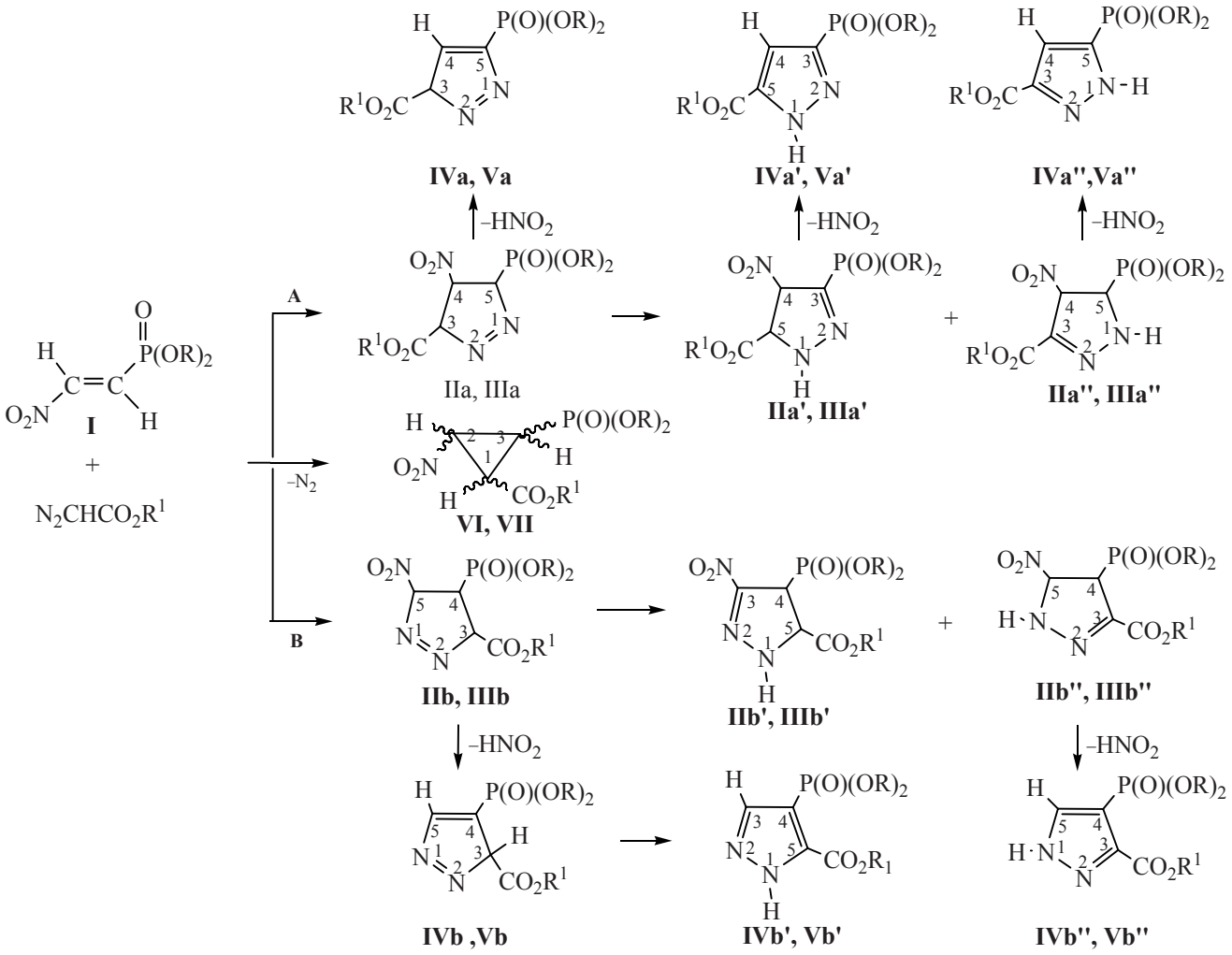
The chemistry of dialkyl 2-nitroethenylphosphonates has been studied mainly on the examples of their reactions with amines and some C- and S-nucleophiles [1, 2]. Earlier we studied reactions of 2-nitroethenylphosphonates with the representatives of a series of acyclic [3, 4] and cyclic dienes [5–8] as well as with some of 1,3-dipoles: phenyl azide [9], sodium azide [10], and phenyldiazomethane [11]. The reactions of 1,3-dipolar cycloaddition of 2-nitroethenylphosphonates with diazoacetic ester have not been studied so far. However, there are publications concerning reactions of vinylphosphonates, their predecessors, with azides [12] and diazo compounds [13–16]. According to these investigations vinylphosphonates reacted with diazomethane, diphenyldiazomethane, and diazoacetic esters regeoselectively with the initial formation of $\Delta^1$-pyrazolines that under reaction conditions underwent prototropic isomerization forming thermodynamically more stable $\Delta^2$-pyrazolines differing by the location of azomethine fragment either at phosphonate or at carboxylate function [15].

In this work we studied a reaction of 2-nitroethenylphosphonate (**I**) with alkyldiazoacetates. By the data [17–19] diazoacetic ester is a stable compound and is capable of entering in 1,3-dipolar cycloaddition at 95–100ºC only. However, in our case this reaction proceeded even at room temperature and required 6–10 days for the completion. Note that introduction of a nitro group to the vicinal position of vinylphosphonate promoted the attack by the 1,3-dipole (ethyl or methyl diazoacetate) on both carbon atoms of the dipolarophile (**I**) C=C bond and initiated the reaction in two competing directions (**A** and **B**) with the formation of regioisomeric $\Delta^1$-pyrazolines (**IIa, IIb, IIIa, IIIb**). The presence in the molecule of three electron-withdrawing groups simultaneously leads to a series of intramolecular transformations: prototropic isomerization with the formation of tautomeric forms of $\Delta^2$-pyrazolines (**IIa', IIb', IIa'', IIb'', IIIa', IIIb', IIIa'', IIIb''**), and denitration leading to respective $\Delta^1$-(**IVa, IVb,Va, Vb**) and $\Delta^2$-(**IVa', IVb', IVa'', IVb'', Va', Vb', Va'', Vb''**) pyrazoles. From the reaction mixture besides the adducts of 1,3-dipolar cycloaddition, pyrazolines and pyrazoles cyclopropane derivatives **VI**, **VII** were isolated as mixtures of diastereomers.

By varying conditions of the reaction between dipolarophile **I** and ethyldiazoacetate (Table 1) we succeeded to show that in ether at 0–5ºC are formed preferably $\Delta^2$-pyrazolines (with the ratio of $\Delta^2$-pyrazoline **IIa'**:**IIb'** = 1:1.5). The higher reaction




R = $C_2H_4Cl$: (**I, IIa, IIa', IIa'', IIb, IIb', IIb''–Va, Va', Va'', Vb, Vb', Vb'', VI, VII**); $R^1$ = Et: (**IIa, IIa', IIa'', IIb, IIb', IIb'', IVa, IVa', IVa'', IVb, IVb', IVb'', VI**); $R^1$ = Me: (**IIIa, IIIa', IIIa'', IIIb, IIIb', IIIb'', Va, Va', Va'', Vb, Vb', Vb'', VII**).

temperature, 20–35°C (in ether), naturally led to an increase in the yield of $\Delta^2$-pyrazoles (62–65%) present as tautomeric forms (**IVa, IVa'', IVb', IVb''**). Use of more polar solvents ($CH_2C1_2$, $CHC1_3$, 20°C) resulted in the predominant formation of $\Delta^2$-pyrazoles and in the increased yield of cyclopropanes from 8 to 22%. Note that therewith the **B** pathway predominates, as attested by the data of $^1H–\{^{31}P\}$ NMR spectroscopy and reflected in the yields (40–48%) of isolated $\Delta^2$-pyrazoles (**IVb', IVb''**) (the ratio of $\Delta^2$-pyrazoles **IVb'**:**IVb''**=1:10). The significant domination of **B** pathway (in particular in the reaction in $CH_2C1_2$, 20°C) allowed the formation of the major products, pyrazoles **IVb'** and **IVb''**, as a tautomeric mixture.

The significant effect of the solvent polarity on the predominance of one pathway, **A** or **B** (in our case it is **B** pathway) indicates complete or partial realization of the non-concerted mechanism of the reaction of diazoacetic ester with dipolarophiles **I** [20, 21].

Compounds (**IIa', IIb'–Va', Vb', IVa'', IVb'', Va'', Vb''**) were isolated by column chromatography as pairs of regioisomers, cyclopropanes (**VI,VII**) as a mixture of diastereomers, $\Delta^1$-(**IIa, IIb, IIIa, IIIb**), and $\Delta^2$-pyrazolines (**IIa'', IIb'', IIIa'', IIIb''**), and $\Delta^1$-pyrazoles (**IVa, IVb, Va, Vb**) were registered as a mixture of regioisomers and tautomers; compounds (**IVa'', Va'', IVb', Vb'**) were isolated individualy.

Structures of the obtained series of $\Delta^1$-(**IIa, IIb, IIIa, IIIb**) and $\Delta^2$-(**IIa', IIb', IIa'', IIb'', IIIa', IIIb', IIIa'', IIIb''**) pyrazolines were established on the basis of their spectral characteristics ($^1H$, $^{31}P$ NMR and IR

**Table 1.** Yields and ratios of products obtained by reaction of 2-nitroethenylphosphonate (**I**) with diazoacetic ether under various conditions

| Conditions | | | Yield, % | | | | |
|---|---|---|---|---|---|---|---|
| solvent | *T*, °C | duration, days (h) | $\Delta^2$-Pyrazolines **II** | | $\Delta^2$-Pyrazolines **IV** | | Cyclopropane **VI** |
| | | | **a', b', a'', b''** | **a':b'** ratio | **a', b', a'', b''** | **a':b'** ratio | |
| Ether | 0–5 | 10 | 46 | 1:1.5 | 15[a] | 1:1 | 8[b] |
| | 20 | 7 | 12[b] | 0.9:1.2 | 62 | 1:1 | 10[b] |
| | 35 | (3) | 5[b] | – | 65 | 1:2 | 12[b] |
| $CH_2Cl_2$[a] | 20 | 10 | 13 | 1:10 | 56 | 1:10 | 15 |
| $CHCl_3$ | 20 | 10 | 10[b] | 1:9 | 45 | | 22[b] |

[a] In $CH_2Cl_2$ mainly the pyrazoles **IVb'**, **IVb''** were obtained. [b] Yield after repeated chromatography.

spectroscopy) by comparison with the published data for structurally related compounds [22, 23]. Formation of pyrazolines and pyrazoles as pairs of regioisomers and tautomers was shown by the duplication of the signals of the ring protons and the signals of phosphonate, carboxylate, and amino groups in $^1$H NMR spectra of these compounds and of the signals of phoshorus nuclei in $^{31}$P NMR spectra.

IR spectra of the obtained series of phosphorylated pyrazolines and pyrazoles contain characteristic bands of all functional groups. IR spectra of compounds (**IIa, IIa', IIa'', IIb, IIb', IIb''–Va, Va', Va'', Vb, Vb', Vb''**) contain absorption bands at 1290–1250 (P=O) and 1130–1070, 1030–1025 $cm^{-1}$ (P–O–C) corresponding to the phosphonate function. The ester groups of these compounds give rise to strong bands at 1740–1735 (C=O) and 1190–1160, 1030–1010 $cm^{-1}$ (C–O–C). The vibration bands of non-conjugated nitro groups in pyrazolines (**IIa, IIb, IIIa, IIIb, IIa', IIa'', IIb'', IIIa', IIIa'', IIIb''**) are observed at 1580–1560 and 1380–1360 $cm^{-1}$, and conjugated nitro group in compounds (**IIb', IIIb'**) give rise to bands at 1545–1520 and 1360–1330 $cm^{-1}$. The stretching vibrations of NH group in the studied pyrazolines and pyrazoles appear as bands in the regions of 3420–3385 and 3130–3120 $cm^{-1}$.

The analysis of $^1$H, $^{31}$P NMR spectra of the obtained pyrazolines in combination with the data of IR spectra and in comparison with the appropriate characteristics of the structurally related compounds described in the literature [22, 23], allowed to state that they belong to $\Delta^1$-(**IIa**, **IIb**, **IIIa**, **IIIb**) and $\Delta^2$-(**IIa'**, **IIb'**, **IIa''**, **IIb''**, **IIIa'**, **IIIa''**, **IIIb''**) forms (Tables 2, 3).

In favor of the $\Delta^1$-structure of pyrazolines **IIa, IIb, IIIa, IIIb** testifies the nature and range of appearance of the methine protons signals ($C^3$H, $C^4$H, $C^5$H) of heterocycle (Table 2). As the analytical criterion for the assignment of regioisomers to the structure **a** or **b** we used the comparison of the values of chemical shifts of the methine protons of the ring at $C^{3–5}$, which depend on the influence of adjacent functional groups (nitro, carboxylate, phosphonate), and also on their proximity to N=N bond. Thus, in the spectra of regioisomers **IIa, IIIa** the ring protons give rise to a broad multiplet at 6.00 ppm, while for the isomers **IIb, IIIb** this range is enlarged from 4.85 to 6.30 ppm due to the effect of electron-withdrawing N=N group on the nitromethine proton $C^5$H of compounds **IIb, IIIb**. The chemical shift of this proton in the isomers **IIb, IIIb** equals 6.30 ppm, hence it undergoes downfield shift as compared with ($C^4$H) in the regioisomers **IIa**, **IIIa** where the respective chemical shift equals 6.00 ppm. In regioisomers **IIa**, **IIIa** the $C^3$H proton that is affected by the adjacent electron-withdrawing nitro group gives a signal at lower field (6.00 ppm) than the related $C^3$H proton in the isomers **IIb, IIIb**, more distant from the nitro group (4.85–4.90 ppm) (Table 2).

The values of phosphorus chemical shift (19.2–21.0 ppm) in $^{31}$P NMR spectra of comounds **IIa**, **IIb**, **IIIa**, **IIIb** that correspond to location of phosphonate group at $sp^3$-hybridized carbon atom are consistent with their $\Delta^1$ structures [21].

Regioisomeric $\Delta^2$-pyrazolines (**IIa', IIb', IIIa', IIIb'**) and their tautomers **IIa'', IIb'', IIIa'', IIIb''** differ from each other by the location at their azomethine fragment of either nitro, or dialkoxyphosphoryl, or alkoxycarbonyl function [–$HN^1$–$N^2$=$C^3$–$CO_2$R (**IIa'', IIb'', IIIa'', IIIb''**), –$HN^1$–$N^2$=$C^3$–$NO_2$ (**IIb', IIIb'**), $HN^1$–$N^2$=$C^3$–P(O)$(OR)_2$ (**IIa'**, **IIIa'**)]. In the $^{31}$P NMR spectra of the mixture of regioisomeric and tautomeric pyrazolines **IIa', IIb', IIa'', IIb'', IIIa', IIIb', IIIa'', IIIb''** the signals of

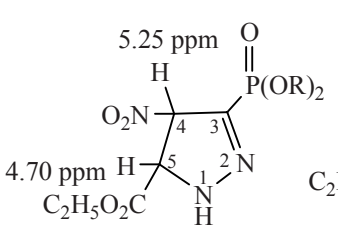
**Table 2.** Data of $^{1}H$, $^{31}P$ NMR spectra (δ, ppm, *J*, Hz, $CDCl_3$) of nitropyrazoline phosphonates **IIa**, **IIb**, **IIIa**, **IIIb** and **IIa'**, **IIa''**, **IIb'**, **IIb''**, **IIIa'**, **IIIa''**, **IIIb'**, **IIIb''**

| Comp. no. | $^{1}H$ NMR spectra, δ, ppm, *J*, Hz ($CDCl_3$) | | | | | | | $^{31}P$ |
|---|---|---|---|---|---|---|---|---|
| | $C^4H$ ($C^3H$) | $C^5H$ | $P(O)(OR)_2$ | | $CO_2R$ | | NH | |
| | | | $OCH_2$ | $CH_2Cl$ | $OCH_2$ | $CH_3$ | | |
| **IIa** | 6.00 m | | 4.35 q | 3.70 t | 4.20 q | 1.35 t | – | 20.0 |
| **IIb** | 5.60 m (4.90 m) | 6.30 m | 4.35 q | 3.70 t | 4.30 q | 1.35 t | – | 19.2 |
| **IIIa** | 6.00 m | | 4.38 q | 3.70 t | – | 3.85 s | – | 21.0 |
| **IIIb** | 5.60 m (4.85 m) | 6.30 m | 4.35 q | | – | 3.80 s | – | 19.2 |
| **IIa'** | 5.25 | 4.70 | 4.40 q | 3.72 t | 4.25 q | 1.35 t | 8.70 s | 14.0 |
| | $^{3}J_{4,5}$ 7.0, $^{3}J_{HP}$ 8.0 | | | | | | | |
| **IIb'** | 4.60 m | 4.65 | 4.38 q | 3.70 t | 4.30 q | 1.35 t | | 19.0 |
| | $^{3}J_{4,5}$ 6.8, $^{3}J_{HP}$ 9.0, $^{2}J_{HP}$ 18.0 | | | | | | | |
| **IIIa'** | 5.35 | 5.03 | 4.40 q | 3.76 t | – | 3.83 s | 8.18 s | 13.8 |
| | $^{3}J_{HP}$ 8.0, $^{3}J_{4,5}$ 7.0 | | | | | | | |
| **IIIb'** | 4.40 m | 4.45 m | 4.35 q | 3.72 t | – | 3.92 s | 7.70 s | 18.0 |
| **IIa''** | 5.38 | 5.15 | 4.40 q | 3.70 t | 4.40 q | 1.40 t | 7.90 s | 16.0 |
| | $^{3}J_{4,5}$ 6.5, $^{3}J_{HP}$ 8.0, $^{2}J_{HP}$ 16.0 | | | | | | | |
| **IIb''** | 4.40 m | 6.73 | 4.40 q | 3.73 t | 4.40 q | 1.40 t | 8.10 s | 15.7 |
| | $^{3}J_{4,5}$ 6.6, $^{3}J_{HP}$ 9.1 | | | | | | | |
| **IIIa''** | 5.68 | 5.20 | 4.38 q | 3.70 t | – | 3.82 s | 7.80 s | 16.5 |
| | $^{3}J_{HP}$ 8.0, $^{3}J_{4,5}$ 6.0 | | | | | | | |
| **IIIb''** | 4.40 m | 6.70 | 4.40 q | 3.72 t | – | 3.92 s | 8.30 s | 15.8 |
| | $^{3}J_{4,5}$ 6.8, $^{3}J_{HP}$ 9.3 | | | | | | | |

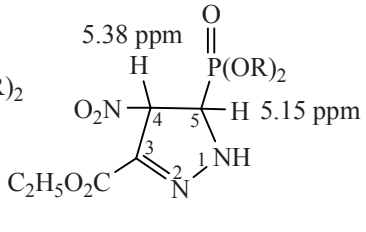
**Table 3.** Data of $^{1}H$, $^{31}P$ NMR spectra (δ, ppm, *J*, Hz, $CDCl_3$) of nitropyrazole phosphonates **IVa**, **IVb**, **Va**, **Vb** and **IVa'**, **IVa''**, **IVb'**, **IVb''**,**Va'**, **Va''**, **Vb'**, **Vb''**

| Comp. no. | $^{1}H$ NMR spectra, δ, ppm, *J*, Hz ($CDCl_3$) | | | | | | | $^{31}P$ |
|---|---|---|---|---|---|---|---|---|
| | $C^3H$ | $C^4H$ ($C^5H$) | $P(O)(OR)_2$ | | $CO_2R$ | | NH | |
| | | | $OCH_2$ | $CH_2Cl$ | $OCH_2$ | $CH_3$ | | |
| **IVa** | 5.25 d | 6.57 d | 4.40 q | 3.73 t | 4.40 q | 1.37 t | - | 13.0 |
| | $^{3}J_{3,4}$ 1.5 | $^{3}J_{3,4}$ 1.5 | | | | | | |
| **IVb** | 5.35 s | (7.78 s) | 4.40 q | 3.72 t | 4.40 q | 1.37 t | - | 12.8 |
| **Va** | 5.25 d | 6.59 d | 4.40 q | 3.76 t | – | 3.88 s | - | 15.0 |
| | $^{3}J_{3,4}$ 1.5 | $^{3}J_{3,4}$ 1.5 | | | | | | |
| **Vb** | 5.35 s | (7.75 s) | 4.40 q | 3.72 t | | 3.91 s | - | 14.2 |
| **IVa'** | – | 7.25 s | 4.40 q | 3.74 t | 4.36 q | 1.40 t | 14.0 s | 13.5 |
| **IVb'** | 8.20 s | – | 4.40 q | 3.72 t | 4.40 q | 1.40 t | 8.22 s | 12.0 |
| **Va'** | – | 7.27 s | 4.30 q | 3.76 t | – | 3.92 s | 13.2 s | 13.8 |
| **Vb'** | 8.20 s | – | 4.40 q | 3.72 t | – | 3.96 s | 8.40 s | 12.0 |
| **IVa''** | – | 7.38 s | 4.40 q | 3.72 t | 4.40 q | 1.40 t | 10.6 s | 13.0 |
| **IVb''** | – | (7.55 s) | 4.40 q | 3.73 t | 4.40 q | 1.40 t | 8.75 s | 12.5 |
| **Va''** | – | 7.27 s | 4.40 q | 3.73 t | – | 3.98 s | 12.4 s | 13.8 |
| **Vb''** | – | (7.60 s) | 4.40 q | 3.70 t | | 4.00 s | 8.75 s | 12.4 |

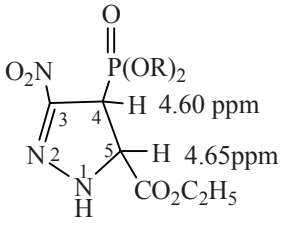
phosphorus nuclei are present at 13.8–14.0 ppm, corresponding to the location of phosphoryl group at the $sp^2$-hybridized carbon atom in the isomers **IIa', IIIa'**, and at 15.7–19.0 ppm, corresponding to phosphorus atom at the $sp^3$-hybridized carbon atom (isomers **IIb', IIa'', IIb'', IIIb', IIIa'', IIIb''**)] [24].



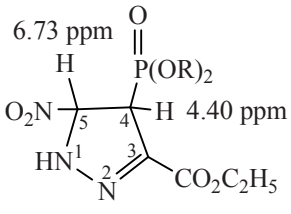

**IIa'**




**IIa''**




**IIb'**




**IIb''**

These regioisomers are better distinguishable by means of $^1$H NMR spectroscopy. For the identification of regioisomeric $\Delta^2$-pyrazolines we used the signals of NH and methine protons in the ring that suffer the influence of C=N bond and functional groups.

The ring proton $C^5H$ near the alkoxycarbonyl function in compound **IIb'** gives a signal at 4.65 ppm, while in the spectrum of **IIa'** isomer due to the influence of the neighboring nitro group its signal undergoes a downfield shift (4.70 ppm).

The methine proton near phosphonate group in compound **IIa''** resonates downfield (5.15 ppm) as compared with the $C^4H$ proton in **IIb'** (4.60 ppm) because of the electron-acceptor effect of heterocyclic nitrogen atom $N^1$. The analogous signal of methine proton in **IIb''** tautomer is shifted upfield (4.40 ppm) because the electron-withdrawing effect of C=N bond with carboxylate substituent ($RO_2C$–C=N) is weaker than in the case of N=C fragment with $NO_2$ group in **IIb'**. The nitromethine proton in tautomers **IIa', IIa''** gives a signal at 5.25, 5.38 ppm, while in the spectrum of tautomer **IIb''** its signal is shifted downfield (6.73 ppm) due to the influence of $N^1$ atom in the heterocycle.

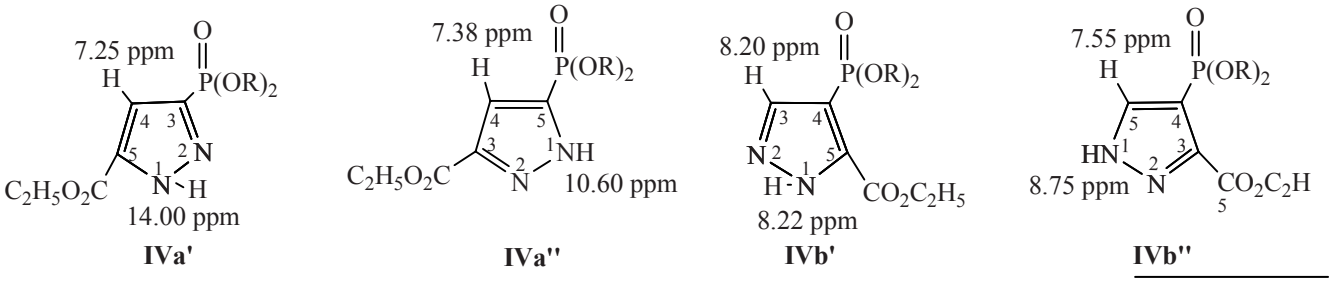
The regioisomers $\Delta^1$-pyrazoles (**IVa, IVb, Va, Vb**) were identified by the comparison of chemical shifts of methine protons $C^3H$ contiguous to the ester group and located at 5.25 and 5.35 ppm (Table 3). Chemical shift of $C^3H$ protons in **b** isomers (5.35 ppm) as compared with **a** isomers corresponding to a lower field is evidently due to the stronger effect of the closely located phosphonate function.

Spectral characteristics of the ring olefin protons are also informative; at their analysis we take into the consideration their distances from the N=N bond. The signals of $C^4H$ olefin proton in the **a** structures **IV**, **V** have chemical shifts 6.57 and 6.59 ppm, respectively; in related **b** structures they are shifted downfield to 7.78 and 7.75 ppm due to the effect of N=N group. The phosphorus signals in the $^{31}$P NMR spectra of regioisomers **IVa, IVb** give signals at 13.0 and 12.8 ppm indicating the location of the phosphoryl group at the $sp^2$-hybridized carbon atom.

The principal analytic criteria for assignment certain structure to $\Delta^2$-pyrazoles (**IVa, IVa', IVa'', IVb, IVb'', IVb'', Va, Va', Va'', Vb, Vb', Vb''**) are the values of chemical shift of olefin protons, the protons of amino group, and of phosphorus nuclei (Table 3). The $^1$H NMR spectra of these pyrazoles are fairly complicated due to the formation of not only of isomers but also of tautomers (this is true practically for all five-membered heterocycles). For the identification we used the $^1$H NMR spectra of the samples containing analytically pure pairs of regioisomers or tautomers.

For the isomers **a'**, **a''** where P=O and C=O groups are the most distant the large downfield shifts of the protons of amino group (10.60–14.00 ppm) are characteristic. This is a consequence of the effect of C=N group neighboring to the electron-withdrawing alkoxycarbonyl or dialkoxyphosphoryl functions (structure **a'**), or of C=N bond and electron-acceptor substituent at the C=C bond (structure **a''**).

In regioisomers **IVb', IVb'', Vb', Vb''** these effects are absent, therefore the signsls of NH protons occur at higher field 8.22–8.75 ppm. Similar regularity for the protons of the ring NH group has been noted for $\Delta^2$-pyrazoles [25]. In the $^1$H NMR spectrum of a mixture of regioisomeric $\Delta^2$-pyrazoles **IVa', IVb'** isolated together the olefinic proton ($C^3H$) of the isomer **IVb'** is affected by the C=N bond and resonates downfield




**IVa'** **IVa''** **IVb'** **IVb''**

(8.20 ppm) as compared with the related proton ($C^4H$) in **IVa''** regioisomer (7.25 ppm).

In the tautomeric mixture of $\Delta^2$-pyrazole derivatives **IVb'**, **IVb''** (that was obtained by keeping at 18°C compound **IVb'** isolated in the individual state from the mixture of regioisomers **IVa', IVb'**) we assigned the signals of olefin protons at 8.20 and 7.55 ppm to tautomers **IVb'** and **IVb''**, respectively (Fig. 1). The appearance of the signal of $C^5H$ proton ($N^1$–$C^5H$=$C^4$) of pyrazole **IVb''** downfield compared to the signal of $C^3$–$C^4H$=$C^5$ proton in (**IVa'**) is caused by the effect of the neighboring $N^1$ heteroatom. The obtained values of chemical shifts of olefin protons in **IVa', IVb', IVb''** were taken into account in the analysis of $^1H$ NMR spectra of the mixture of all isomers of $\Delta^2$-pyrazole (**IV**). In this spectrum the signals were registered at 8.20, 7.55 and 7.25 ppm (of the isomers **IVa', IVb', IVb''**) and a singlet at 7.38 ppm that we assigned to the remaining isomer **IVa''**.

Additional crystallization of tautomers **IVb', IVb''** from methanol provided individual tautomer **IVb''**. Its structure was unequivocally established by X-ray structural analysis. The geometry of the molecule is shown in Fig.2, the atomic coordinates and geometric parameters of the molecule are listed in Tables 4 and 5.

The coincidence of the result obtained by X-ray analysis with the conclusions based on $^1H$ and $^{31}P$

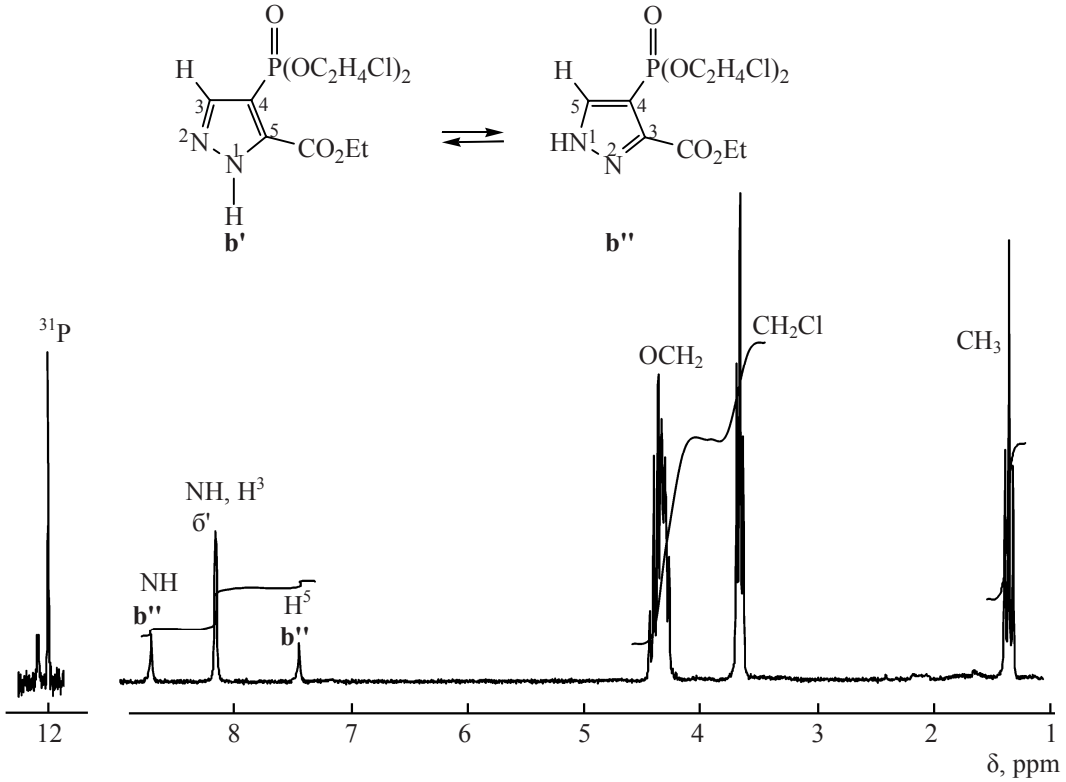



**Fig. 1.** $^1H$ NMR spectrum of ethyl-4-bis(2-chloroethoxy)phosphoryl-1*H*-pyrazol-5(3)-yl carboxylates (**IVb'**, **IVb''**) in $CDCl_3$.

**Table 4.** Atomic coordinates of structure **IVb''**, equivalent thermal parameters ($\times 10^4$), and isotropic parameters ($Å^2 \times 10^3$) of non-hydrogen atoms

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| $P^1$ | 7888(1) | –1563(1) | 6845(1) | 43(1) |
| $Cl^1$ | 5136(2) | –1605(1) | 9809(1) | 94(1) |
| $Cl^2$ | 11269(2) | 360(1) | 8922(2) | 128(1) |
| $O^2$ | 6784(2) | –1547(2) | 7667(2) | 50(1) |
| $O^1$ | 8237(2) | –2610(2) | 6600(2) | 56(1) |
| $O^3$ | 9025(2) | –928(2) | 7529(2) | 56(1) |
| $O^8$ | 4597(2) | –1668(2) | 3526(2) | 57(1) |
| $C^6$ | 6364(3) | –916(2) | 4671(3) | 40(1) |
| $N^5$ | 6223(3) | –88(2) | 3996(2) | 49(1) |
| $N^4$ | 7122(3) | 563(2) | 4501(3) | 53(1) |
| $C^7$ | 5561(3) | –1832(2) | 4389(3) | 46(1) |
| $O^7$ | 5775(3) | –2634(2) | 4867(3) | 67(1) |
| $C^2$ | 7368(3) | –786(2) | 5623(3) | 41(1) |
| $C^3$ | 7813(3) | 186(2) | 5458(3) | 50(1) |
| $C^8$ | 3764(4) | –2536(3) | 3206(4) | 75(1) |
| $C^{10}$ | 6275(3) | –619(3) | 8120(3) | 54(1) |
| $C^{11}$ | 4994(4) | –832(3) | 8528(3) | 61(1) |
| $C^9$ | 2733(4) | –2221(4) | 2248(4) | 78(1) |
| $C^{12}$ | 10348(4) | –1133(4) | 7437(5) | 89(2) |
| $C^{13}$ | 11183(5) | –913(5) | 8532(6) | 106(2) |

NMR spectroscopy not only confirmed unequivocally the structure of compound **IVb''** as the isomer with orientation to the same side of dialkoxyphosphoryl and ethoxycarbonyl groups but also proved reliably that the functionalized pyrazolines with carboxylate and phosphonate groups were prone to tautometric transformations.

By the data of X-ray structural analysis, the pyrazole ring of **IVb''** molecule is planar within the experimental error of 0.0010(2) Å, the respective torsion angles in the ring are: $C^2C^6N^5N^4$ 0.2(3)º, $C^6N^5N^4C^3$ –0.2(3)º, $N^5C^6C^2C^3$ –0.1(4)º, $N^5N^4C^3C^2$ 0.1(4)º. The analysis of bond lengths indicates substantial delocalization of π-electron density over the ring, as seen from the equalization of bonds $C^3$–$N^4$, $N^4$–$N^5$ and $N^5$–$N^6$ [the respective bond lengths are 1.333(4), 1.343(4) and 1.337(4) Å], and from some elongation of $C^2$=$C^3$ double bond, to 1.382(4) Å. The whole planar ethoxycarbonyl group is slightly turned relatively to the pyrazole ring: the $C^2C^6C^7O^7$ torsion angle equals –9.3(6)º. This conformation of the substituent can be defined by the conjugation of

**Table 5.** Bond lengths (*d*, Å), bond angles (ω, deg), and torsion angles (τ, deg) in structure **IVb''**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| $P^1$–$O^1$ | 1.462(2) | $C^6$–$C^2$ | 1.423(4) |
| $P^1$–$O^2$ | 1.565(3) | $C^6$–$C^7$ | 1.479(4) |
| $P^1$–$O^3$ | 1.571(2) | $N^5$–$N^4$ | 1.343(4) |
| $P^1$–$C^2$ | 1.769(3) | $N^4$–$C^3$ | 1.333(4) |
| $Cl^1$–$C^{11}$ | 1.782(4) | $N^4$–$H^4$ | 0.8600 |
| $Cl^2$–$C^{13}$ | 1.738(6) | $C^7$–$O^7$ | 1.200(4) |
| $O^2$–$C^{10}$ | 1.453(4) | $C^2$–$C^3$ | 1.382(4) |
| $O^3$–$C^{12}$ | 1.408(5) | $C^3$–$H^3$ | 0.9300 |
| $O^8$–$C^7$ | 1.333(4) | $C^8$–$C^9$ | 1.493(6) |
| $O^8$–$C^8$ | 1.451(4) | $C^{10}$–$C^{11}$ | 1.481(5) |
| $C^6$–$N^5$ | 1.337(4) | $C^{12}$–$C^{13}$ | 1.465(7) |
| Angle | ω, deg | Angle | ω, deg |
| $O^1P^1O^2$ | 110.05(15) | $N^5C^6C^2$ | 111.4(3) |
| $O^1P^1O^3$ | 114.42(13) | $N^5C^6C^7$ | 121.4(3) |
| $O^2P^1O^3$ | 104.17(13) | $C^2C^6C^7$ | 127.1(3) |
| $O^1P^1C^2$ | 116.88(14) | $C^6N^5N^4$ | 104.5(2) |
| $O^2P^1C^2$ | 107.36(13) | $C^3N^4N^5$ | 113.0(3) |
| $O^3P^1C^2$ | 102.92(14) | $O^7C^7O^8$ | 124.2(3) |
| $C^{10}O^2P^1$ | 123.3(2) | $O^7C^7C^6$ | 123.5(3) |
| $C^{12}O^3P^1$ | 122.1(3) | $O^8C^7C^6$ | 112.2(3) |
| $C^7O^8C^8$ | 115.2(3) | $C^3C^2C^6$ | 103.3(3) |
| $C^3C^2P^1$ | 124.9(2) | $O^8C^8C^9$ | 108.3(3) |
| $C^6C^2P^1$ | 131.5(2) | $O^2C^{10}C^{11}$ | 109.2(3) |
| $N^4C^3C^2$ | 107.8(3) | $C^{10}C^{11}Cl^1$ | 112.5(3) |
| $O^3C^{12}C^{13}$ | 111.8(5) | $C^{12}C^{13}Cl^2$ | 114.7(4) |
| Angle | τ, deg | Angle | τ, deg |
| $O^1P^1O^2C^{10}$ | 176.6(2) | $C^7C^6N^5N^4$ | –178.5(3) |
| $O^3P^1O^2C^{10}$ | 53.5(3) | $C^6N^5N^4C^3$ | –0.2(4) |
| $C^2P^1O^2C^{10}$ | –55.2(3) | $C^8O^8C^7O^7$ | 1.8(5) |
| $O^1P^1O^3C^{12}$ | 28.3(4) | $C^8O^8C^7C^6$ | –179.8(3) |
| $O^2P^1O^3C^{12}$ | 148.6(4) | $N^5C^6C^7O^7$ | 169.1(3) |
| $C^2P^1O^3C^{12}$ | –99.5(4) | $C^2C^6C^7O^7$ | –9.3(6) |
| $C^2C^6N^5N^4$ | 0.2(3) | $N^5C^6C^7O^8$ | –9.3(4) |
| $C^7C^6C^2C^3$ | 178.5(3) | $C^2C^6C^7O^8$ | 172.2(3) |
| $N^5C^6C^2P^1$ | 173.9(2) | $N^5C^6C^2C^3$ | –0.1(4) |
| $C^7C^6C^2P^1$ | –7.5(5) | $O^1P^1C^2C^6$ | 54.4(3) |
| $O^1P^1C^2C^3$ | –132.7(3) | $O^2P^1C^2C^6$ | –69.7(3) |
| $O^2P^1C^2C^3$ | 103.1(3) | $O^3P^1C^2C^6$ | –179.3(3) |
| $O^3P^1C^2C^3$ | –6.5(3) | $N^5N^4C^3C^2$ | 0.1(4) |
| $P^1O^2C^{10}C^{11}$ | 161.8(2) | $C^6C^2C^3N^4$ | 0.0(4) |
| $O^2C^{10}C^{11}Cl^1$ | 69.3(3) | $P^1C^2C^3N^4$ | –174.5(2) |
| $P^1O^3C^{12}C^{13}$ | –147.4(4) | $C^7O^8C^8C^9$ | 179.2(3) |
| $O^3C^{12}C^{13}Cl^2$ | –66.1(6) | | |

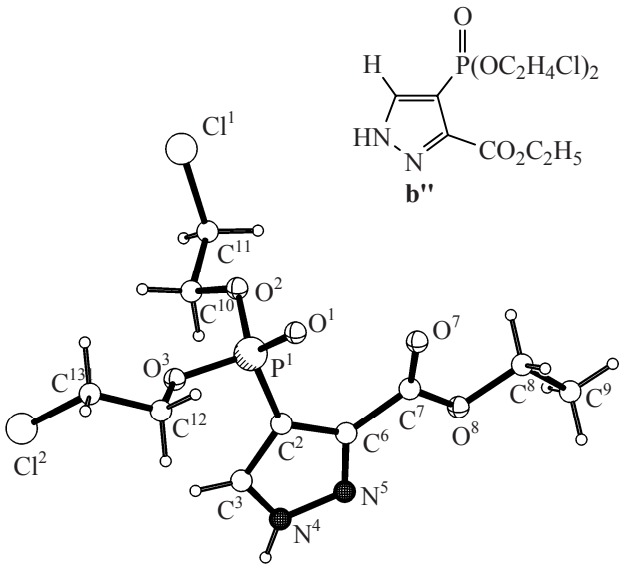



**Fig. 2.** Molecular geometry of compound **IVb''** in crystal.

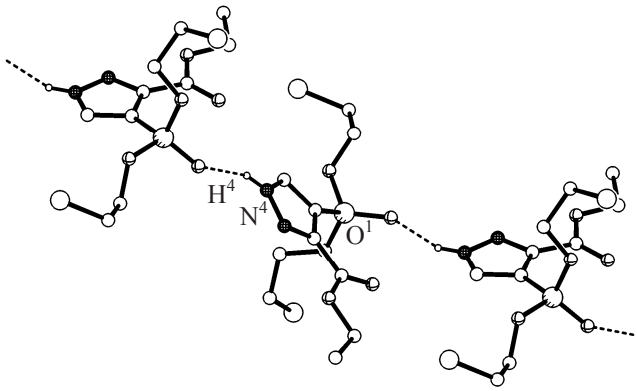



**Fig. 3.** Formation of chain of hydrogen-bound molecules in crystal of compound **IVb''**. Only the hydrogen atoms involved to hydrogen bonds (dashed) are shown.

carbonyl group with the aromatic ring π-system. The conformation at the $C^2$–$P^1$ bond is also eclipsed: the $O^3P^1C^2C^3$ torsion angle equals –6.5(3)°. The observed conformation of substituents is probably defined by steric factors because the bulky substituents are in the *ortho* position (that is, at the neighboring carbon atoms of the conjugated cyclic fragment). This assumption is confirmed by the the fact that the exocyclic bond angles $C^6C^2P^1$ and $C^2C^6C^7$ are increased to 131.5(2) and 127.1(3)°, respectively.

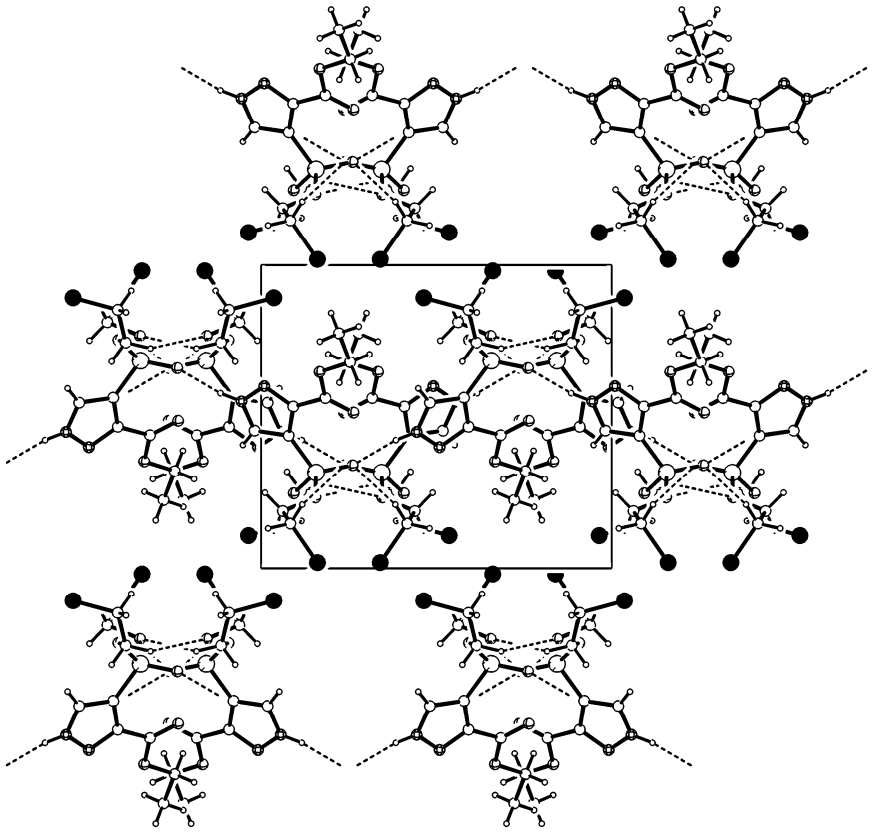


**Fig. 4.** Bilayer supramolecular structure of compound **IVb''** in crystal.

In the crystal of compound **IVb''** there are intra- and intermolecular interactions of various types, including classical N–H···O and rather weak C–H···O and C–H···Cl bonds (Fig. 3). Among the intramolecular interactions we have to note the interaction of oxygen atom $O^1$ in the phosphoryl function with the methylene hydrogen $H^{122}$. The parameters of the contact are as forllows: $d[C^{12}\cdots O^1]$ 2.992(5)Å, $d[H^{122}\cdots O^1]$ 2.52 Å, $\angle[C^{12}–H^{122}\cdots O^1]$ 110º. Among the intermolecular contacts we have to emphasize first of all the hydrogen bond $N^4–H^4\cdots O^{1'}$. By such bonding the molecules of the compound form infinite zig–zag type chains along the crystallographic axis 0*y* (Fig.3). The bond parameters are: $d[N^4\cdots O^{1'}]$ 2.726(4)Å, $d[H^4\cdots O^{1'}]$ 1.92Å, $\angle[N^4–H^4\cdots O^{1'}]$ 156°, symmetry operation $1/2 - x, -1/2 + y, 1 - z$.

The involvement of hydrogen atoms of methylene groups into hydrogen boning with the oxygen atoms of phosphoryl group and in 2-chloroethoxy substituent leads to binding the mentioned molecular chains in the crystallographic direction *0x* and to the formation of bilayer supramolecular structure (Fig. 4). Parameters of these interactions are: $d[C^{11}\cdots O^{1''}]$ 3.382(4) Å, $d[H^{111}\cdots O^{1''}]$ 2.43 Å, $\angle[C^{11}–H^{111}\cdots O^{1''}]$ 166º, symmetry operation $1/2 + x, 1/2 - y, z$), and $d[C^{12}\cdots O^{1'''}]$ 3.395(6) Å, $d[H^{122}\cdots O^{1'''}]$ 2.55 Å, $\angle[C^{12}–H^{122}\cdots O^{1'''}]$ 145º, symmetry operation $-1/2 + x, 1/2 - y, z$). The chlorine-containing fragments of the molecules are located on the outher sides of the bilayers.

Short contacts between chlorine atoms are not detected, but multiple intermolecular interactions Cl···H are observed of the distances in the range 2.93–3.11 Å. Note that such mutual location of the molecules favors appearance of π–π interactions, but only between the pairs of centrosymmetrical molecules (the distance between ihe centers of the rings 4.17 Å, dihedral angle 0º, the shortest distance between the planes 3.46 Å).

## EXPERIMENTAL

The IR spectra were registered on an Infra-LUM FT-02 spectrometer (from solutions in chloroform, *c* 0.1–0.001 mol $l^{-1}$). The $^1H$ and $^{31}P$ NMR spectra were registered on a Bruker AC-200 spectrometer (200 MHz), solutions in deuterochloroform. Chemical shifts (δ) were measured relative to external reference (HMDS), accuracy ±0.5 Hz. External reference for $^{31}P$ NMR spectra was 85% phosphoric acid. The separation and purification of compounds was carried out by preparative column chromatography on silica gel Chemapol 100/200.

The individuality of compounds and the progress of reaction were monitored by thin layer chromatography on Silufol-254 plates, eluent hexane–acetone, 3:2, development in iodine vapor. The ratio of compounds in mixtures was determined by $^1H$, $^{31}P$ NMR spectroscopy after column chromatography.

X-Ray structural analysis. The crystals of compound **IVb''**, mp 102–104°C, are monoclynic. At 20°C $a$ = 10.315(3), $b$ = 13.189(2), $c$ = 11.490(2) Å, β = 96.97(2)°, $V$ = 1551.6(6) $Å^3$, $d$(calc) 1.477 g $cm^{-3}$, $M$ = 345.11, $Z$ = 4, space group $P2_1/a$. The cell parameters and intensities of 3183 reflexes, among which 2385 have $I \geq 2\sigma$, were measured at 20°C (graphite monochromator, $\lambda Cu K_\alpha$–radiation, ω-scanning, $\theta \leq 74.24°$). Intensity decrese for three test reflexes did not occurred during the experiment. The extinction was taken into account ($\mu Cu = 4.933$ $mm^{-1}$).

The structure was solved by the direct method using SIR program [26] and refined initially in isotropic and then in anisotropic approximation with SHELXL program [27]. Finally from the electron density difference were revealed all hydrogen atoms that in the final least-squares cycles were refined along the *rider* model. Final divergence factors are: $R$ = 0.0601, $R_W$ = 0.1627 over 2385 reflexes with $F^2 \geq 2\sigma$. All the calculations were carried out using MolEN [28] and WinGX [29] programs, images are created with PLATON [30] program. The X-ray structural data are deposited in Cambridge bank of structural data.

The X-ray structural investigation was carried out in the Division of X-ray Structural Investigations of the Center of Collective Exploitation of CKP SAC based on the Laboratory of Diffraction Methods of Investigations, Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of Russian Academy of Sciences. The experiment was carried out on an automatic X-ray diffractometer CAD-4 of NONIUS B.V. firm.

**Ethyl-5(4)-bis(2-chloroethoxy)phosphoryl-4(5)-nitro-4,5-dihydro-3*H*-pyrazol-3-yl carboxylates (IIa, IIb), ethyl-3(4)-bis(2-chloroethoxy)phosphoryl-4(3)-nitro-4,5-dihydro-1*H*-pyrazol-5-yl carboxylates (IIa', IIb'), ethyl-5(4)-bis(2-chloroethoxy)-phosphoryl-4(5)-nitro-4,5-dihydro-1*H*-pyrazol-3-yl carboxylates (IIa'', IIb''), ethyl-5(4)-bis(2-chloroethoxy)phosphoryl-3*H*-pyrazol-3-yl carboxylates (IVa, IVb), ethyl-3(4)-bis(2-chloroethoxy)-**

**phosphoryl-1*H*-pyrazole-5-yl carboxylates (IVa', IVb'), ethyl-5(4)-bis(2-chloroethoxy)phosphoryl-1*H*-pyrazol-3-yl carboxylates (IVa'',b''), ethyl-2- bis(2-chloroethoxy)phosphoryl-3-nitrocyclopropan-1-yl carboxylate (VI).** *a.* To a solution of 1.4 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** in 20 ml of ether was added dropwise 10 ml of ether solution containing 1.14 g of ethyl diazoacetate. The reaction mixture was kept at 20°C for 7 days, the solvent was evaporated, and the residue was subjected to chromatography on silica gel. 0.6 g of the mixture of $\Delta^2$-pyrazolines **IIa', IIb', IIa'', IIb''** and cyclopropane **VI** was isolated (eluent chloroform). From ether 1.07 g (62%) of $\Delta^2$-pyrazoles **IVa', IVb', IVa'', IVb''** was obtained. By repeated chromatography of compounds **IIa', IIb', IIa'', IIb'', VI** with chloroform as eluent 0.18 g (10%) of cyclopropane **VI** was obtained (a mixture of diastereomers), $R_f$ 0.47, 0.42. With ether we isolated 0.24 g (12%) of $\Delta^2$-pyrazolines **IIa', IIb'** (in the ratio 0.9:1), $R_f$ 0.33, 0.18.

By repeated chromatography of pyrazolines **IVa', IVb', IVa'', IVb''** 0.7 g (40%) were isolated regio-isomers **IVa', IVb'** in 1:1 ratio, $R_f$ 0.20, 0.17.

*b.* To a solution of 1.4 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** in 20 ml of ether was added dropwise 10 ml of ether solution containing 1.14 g of ethyl diazoacetate. The reaction mixture was kept at 0–5°C for 10 days, the solvent was evaporated, and the residue was subjected to chromatography on silica gel. 1.30 g of the mixture of $\Delta^1$-(**IIa, IIb**) and $\Delta^2$-pyrazolines **IIa, IIb, IIa', IIb', IIa'', IIb''** and cyclopropane **VI** was isolated (eluent $CHC1_3$). With ether we washed out 0.26 g (15%) of pyrazoles **IVa, IVb, IVa', IVb', IVa'', IVb''**.

By repeated chromatography of compounds **IIa, IIb, IIa', IIb', IIa'', IIb'', VI** with chloroform as eluent 0.15 g (8%) of cyclopropane **VI** was isolated. With ether we isolated 0.90 g (46%) of pyrazolines **IIa, IIb, IIa', IIb', IIa'', IIb''**.

By repeated chromatography of pyrazoles **IVa, IVb, IVa', IVb', IVa'', IVb''** with chloroform as eluent we isolated 0.16 g (9%) of $\Delta^2$-pyrazoles **IVa', IVb'** (1:1 ratio).

By additional chromatography of pyrazolines **IIa, IIb, IIa', IIb', IIa'', IIb''** with chloroform as eluent (first portion, ~100 ml) was isolated 0.45 g (23%) of $\Delta^2$-pyrazolines **IIa'**, **IIb'** [1:1 ratio]. Found, %: C 30.45 30.48; H 4.06 4.09; N 10.34 10.41; P 7.51 7.55. $C_{10}H_{16}Cl_2N_3O_7P$. Calculated, %: C 30.61; H 4.08; N 10.71; P 7.91. From the second portion of chloroform 0.13 g (7%) of $\Delta^2$-pyrazolines **IIa'', IIb''** was isolated [ratio 1.1:1], $R_f$ 0.21, 0.15.

*c.* To a solution of 1.4 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** in 20 ml of ether was added dropwise 10 ml of ether solution containing 1.14 g of ethyl diazoacetate. The reaction mixture was refluxed for 6 h, the solvent was then evaporated, and the residue was subjected to chromatography on silica gel. 0.5 g of mixture of pyrazolines **IIa', IIb', IIa'', IIb''** and cyclopropane **VI** was isolated (eluent $CHC1_3$). With ether we washed out 1.12 g (65%) of $\Delta^2$-pyrazoles **IVa', IVb', IVa'', IVb''**.

By repeated chromatography of compounds **IIa', IIb', IIa'', IIb'', VI** with chloroform as eluent 0.22 g (12%) of cyclopropane **VI** was isolated. With ether we isolated 0.1 g (5%) of pyrazoles **IIa', IIb', IIa'', IIb''**.

*d.* To a solution of 1.4 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** in 20 ml of chloroform, was added dropwise 8 ml of ether solution containing 1.14 g of ethyl diazoacetate and the reaction mixture was kept at 20°C for 10 days. The solvent was evaporated without heating, and the residue was subjected to chromatography on silica gel (eluent $CHC1_3$). 0.8 g of the mixture of pyrazolines **IIa'**, **IIb'**, **IIa''**, **IIb''** and cyclopropane **VI** was isolated. With ether we washed down 0.80 g (45%) $\Delta^2$-pyrazoles **IVa'**, **IVb'**, **IVa''**, **IVb''**.

By repeated chromatography of compounds **IIa'**, **IIb'**, **IIa''**, **IIb''**, **VI** with chloroform as eluent 0.40 g (22%) of cyclopropane **VI** was isolated, with ether, 0.2 g (10%) of pyrazolines **IIa'**, **IIb'** (in 1:9 ratio).

*e.* To a solution of 2 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** in 15 ml of methylene chloride was added dropwise 8 ml of ether solution containing 1.64 g of ethyldiazoacetate. The reaction mixture was kept at 20°C for 10 days. The crystals formed were treated with ether (50×3 ml) and filtered off. 1.07 g (44%) of $\Delta^2$-pyrazoles **IVb'**, **IVb''** was obtained. Found, %: C 34.82, 34.83; H 4.42, 4.39; N 8.13, 8.17; P 9.01, 9.06. $C_{10}H_{15}Cl_2N_2O_5P$. Calculated, %: C 34.78; H 4.34; N 8.11; P 8.98.

By recrystallization from methanol 0.85.g (35%) of compound **IVb''** was isolated, mp 102–104°C. The filtrate and ether extracts were combined, solvents were evaporated, and the residue was subjected to chromatography on silica gel. 0.38 g (15%) of cyclopropane **VI** was isolated (eluent chloroform).

With ether we isolated 0.35 g (13%) of $\Delta^2$-pyrazolines **VIa'**, **VIb'** (in 1:10 ratio). Found, %: C 32.95, 32.99; H 4.38, 4.42; N 3.81, 3.83; P 8.54, 8.58. $C_{10}H_{16}Cl_2NO_7P$. Calculated, %: C 32.97; H 4.40; N 3.85; P 8.52.

From the first portion of methanol (~50 ml) 0.1 g (4%) of pyrazoles **IVa'**, **IVb'**, **IVa''**, **IVb''** was isolated [a mixture of regioisomers and tautomers ]. From the second portion of methanol (~50 ml) 0.2 g (8%) of pyrazoles **IVa'**, **IVb'** (in 1:10 ratio) was isolated. Total yield of pyrazoles **IV** is 1.36 g (56%).

**Methyl-5(4)-bis(2-chloroethoxy)phosphoryl-4(5)-nitro-4,5-dihydro-3*H*-pyrazol-3-yl carboxylates (IIIa, IIIb), methyl-3(4)-bis(2-chloroethoxy)phosphoryl-4(3)-nitro-4,5-dihydro-1*H*-pyrazol-5-yl carboxylates (IIIa', IIIb'), methyl-5 (4)-bis(2-chloroethoxy)phosphoryl-4(5)-nitro-4,5-dihydro-1*H*-pyrazol-3-yl carboxylates (IIIa'', IIIb'')**[)], **ethyl-5(4)-bis(2-chloroethoxy)phosphoryl-3*H*-pyrazol-3-yl carboxylates (Va, Vb), ethyl-3(4)-bis(2-chloroethoxy)phosphoryl-1*H*-pyrazol-5-yl carboxylates (Va', Vb'), ethyl-5(4)-bis(2-chloroethoxy)phosphoryl-1*H*-pyrazol-3-yl carboxylates (Va'', Vb''), ethyl-2-bis(2-chloroethoxy)-phosphoryl-3-nitrocyclopropan-1-yl carboxylate (VII).** The reaction of 1.4 g of bis(2-chloroethyl)-2-nitroethenylphosphonate **I** with methyl diazoacetate was carried out along the procedure *a.* Elution with chloroform afforded 1.30 g of pyrazolines **IIIa**, **IIIb**, **IIIa'**, **IIIb'**, **IIIa''**, **IIIb''** and cyclopropane **VII**, with ether, 0.79 g (48%) pyrazoles **Va**, **Vb**, **Va'**, **Vb'**, **Va''**, **Vb''**. By repeated chromatography of compounds **IIIa**, **IIIb**, **IIIa'**, **IIIb'**, **IIIa''**, **IIIb''**, **V** with chloroform as eluent we isolated 0.21 g (12%) of cyclopropane **VII** (a mixture of diastereomers), $R_f$ 0.38, 0.42. Found, %: C 30.82,30.84; H 3.97, 4.02; N 4.01, 4.05; P 8.81, 8.85. $C_9H_{14}Cl_2NO_7P$. Calculated, %: C 30.86; H 4.00; N 4.00; P 8.86. With ether 0.23 g (12%) pyrazolines **IIIa'**, **IIIb'**, **IIIa''**, **IIIb''** was obtained. Found, %: C 28.55, 28.59; H 3.66, 3.69; N 11.09, 11.13; P 8.15, 8.19. $C_9H_{14}Cl_2N_3O_7P$. Calculated, %: C 28.57; H 3.70; N 11.11; P 8.20.

By repeated chromatography of pyrazoles **Va**, **Vb**, **Va'**, **Vb'**, **Va''**, **Vb''** with chloroform as eluent 0.42 g (25%) of $\Delta^2$-pyrazoles **Va'**, **Vb'** was isolated (1:1 ratio), $R_f$ 0.35, 0.47. Found, %: C 32.63, 32.66; H 3.60, 3.63; N 8.52, 8.54; P 9.36, 9.39. $C_9H_{13}Cl_2N_2O_5P$. Calculated, %: C 32.62; H 3.62; N 8.45; P 9.36.

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